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H/D Exchange Reactions of Methane with Aromatics and Cyclohexane Catalyzed by a Nanoscopic Aluminum Chlorofluoride

Beatriz Calvo,[a] Thomas Braun,*[a] and Erhard Kemnitz*[a]

Dedication ((optional))

Abstract: H/D exchange reactions between methane and deuterated solvents such as bezene-d^6 and cyclohexane-d^{12} are heterogeneously catalysed by a nanoscopic aluminium chlorofluoride (ACF = $AlCl_xF_{3-x}$ $x \approx 0.05$-0.3) under very mild conditions. ^{13}C NMR experiments at labeled methanes reveal the formation of all isotopologues. $AlCl_3$, $AlBr_3$, HS-AlF_3, γ-Al_2O_3 and γ-Al_2O_3 preheated at 700 °C did not show any H/D exchange reaction of methane and benzene-d^6. Mechanistically, an electrophilic activation of methane is suggested at ACF.

Methane is a small and often rather inert molecule that is the major component of natural gas. The abundant reserves of this light hydrocarbon together with the rapid depletion of petroleum reserves have led to an increasing interest in the utilization of methane as energy carrier and feedstock for the production of high value chemicals by the development of new reaction routes in C1 chemistry.[1] The petrochemical industry converts methane on using high energy consuming processes such as steam reforming which leads to an oxidation of the C-H bonds to give mixtures of CO and H_2 from which higher hydrocarbons and their derivatives can be produced.[2] This is a well know industrial technology, but concerning sustainability the stream reforming is an old non-efficient process. Thus, the utilization of methane to its full potential remains a significant challenge for academia and industry.[3]

Some catalytic processes in which methane is oxidized selectively to methanol are based on Shilov-type chemistry.[4] The reactions take place in homogeneous phase and they involve the electrophilic activation of CH_4 at Pt^{II} centers to produce a Pt^{II}-CH_3 species.[5] It is possible to oxidize methane to methyl bisulfate in sulfuric acid with high turnover frequencies (>25,000 h^{-1}), on using K_2PtCl_4 as catalytic precursor. The difficult separation of the product and the recycling of sulfur dioxide preclude the industrial implementation of this important catalytic process.[6]

At a heterogeneous phase, catalytic oxidation of methane has been accomplished by various metal modified zeolites as well as metal oxides.[7] Copéret *et al.* used pre-heated γ-Al_2O_3 at 700°C as one of the most active oxides capable of catalyzing processes to study H/D exchange reactions of CH_4/CD_4 mixtures or D_2/CH_4.[8] There are also reports on oxidative coupling of methane at metal oxides, including its efficient conversion to alkanes[9] or aromatics[10] and although these results are promising, methane activation either in the homogeneous[11] or heterogeneous phase needs further developments of catalytic systems as a well as a deeper understanding of reaction mechanisms.[12]

ACF ($AlCl_xF_{3-x}$ $x \approx 0.05$-0.3) is an amorphous, microporous Lewis-acidic material with a highly distorted structure and a large surface area (> 100 m^2/g), which is capable of catalyzing unique reactions.[13] The conversions involve hydroarylation, hydrodefluorination, hydrodechlorination, dismutation, dehydrofluorination and C-H activation reactions of alkanes.[13] For the latter H/D exchange of cyclic alkanes with deuterated benzene has been achieved.[14] This paper reports H/D exchange catalyzed by ACF under very mild conditions between the aromatics toluene-d^8 or benzene-d^6 and methane, as well as between the two alkanes cyclohexane-d^{12} and methane.

The reaction of benzene-d^6 with $^{13}CH_4$ at 70 °C in screw-capped NMR tubes in the presence of catalytic amounts of ACF gave mono- to fully deuterated methanes as H/D exchange products, as well as tetra- and penta-deuterated benzene (Scheme 1). Likewise, the successful deuteration of methane was accomplished by using toluene-d^8 and reactivity was observed at aromatic C-D bonds and at the CD_3 group. Note that with deuterated benzene the exchange reaction also takes place at room temperature reaching a conversion of 39 % (Table 1). It is remarkable that under the same mild conditions, H/D exchange to methane was also obtained on using cyclohexane-d^{12} as deuterium source. Note further that for the H/D exchange with deuterated cyclohexane, partially deuterated cyclohexane as well as methylcyclohexane were generated; the isomerization of cyclohexane at ACF was described previously.[14]

$$^{13}CH_4 \xrightarrow[\substack{ACF \\ 70\ °C,\ 24\ h}]{solvent} {}^{13}CH_3D + {}^{13}CH_2D_2 + {}^{13}CHD_3 + {}^{13}CD_4$$

$$\text{solvent} = C_6D_6,\ \text{Tol-d}_8,\ C_6D_{12}$$

Scheme 1. H/D exchange between methane and deuterated solvents catalyzed by ACF.

The H/D exchange reactions were monitored by ^1H and ^{13}C NMR spectroscopy, and the results of the catalytic conversions and TOFs are listed in Table 1. In the $^{13}C\{^1H\}$ NMR (inverse-gated decoupled) spectra the signals for the deuterated methane species $^{13}CD_xH_{4-x}$ (x = 1, 2, 3, 4) were integrated to determine their ratios. The spectrum for the exchange reaction with C_6D_6 was compared with a simulated ^{13}C NMR spectrum, which confirms the ratios of the deuterated species (Table 1 and Table S3 (SI)).

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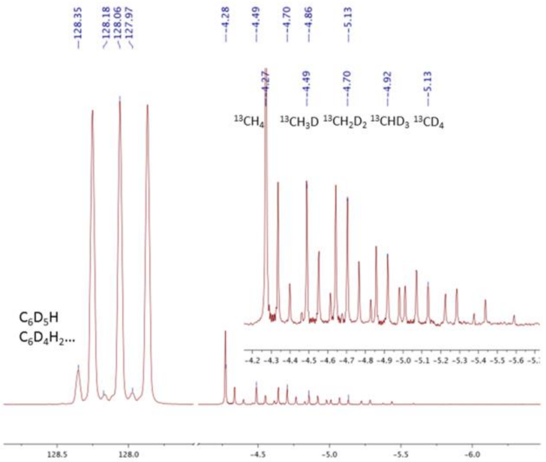


Figure 1. $^{13}C\{^1H\}$ ig NMR spectrum of H/D exchange between methane and benzene-d^6 catalyzed by ACF.

The data in Table 1 also show that the conversions for the deuteration of methane were comparable on using either benzene-d^6 or cyclohexane-d^{12} as deuterium sources, although the reaction times were longer in the case of the cyclic alkane. The activities for the H/D exchange reactions at benzene-d^6, toluene-d^8 and cyclohexane-d^{12} are similar, affording comparable amounts of mono-, di-, tri- and tetra-deuterated methanes for benzene-d^6. Cyclohexane-d^{12} afforded CH_3D and CH_2D_2 as the major species; whereas the use of toluene-d^8 as source of deuterium resulted in CH_3D being the major deuterated methane.

In order to compare the activity of ACF in the H/D exchange reaction of methane with benzene-d^6, we tested other conceivable catalysts such as $AlCl_3$, $AlBr_3$, HS-AlF_3 (high-surface AlF_3) and γ-Al_2O_3 as well as the pre-heated γ-Al_2O_3 at 700 °C. None of these materials were capable of catalyzing the H/D exchange reaction between benzene-d^6 and methane under the same conditions as used for the catalytic reactions at ACF.

Table 1. Deuteration of methane catalyzed by ACF.

entry	solv.	T /ºC	conv /%[a]	TOF (h^{-1})	Products, ratios			
					CH_3D	CH_2D_2	CHD_3	CD_4
1	C_6D_6	25	39	57	-	-	-	-
2	C_6D_6	110	57	83	-	-	-	-
3	C_6D_6	70	77	112	1	0.8	0.8	1.1
4	Tol-d_8	70	82	119	1	0.5	0.4	0.2
5	C_6D_{12}	70	78	113	1	0.8	0.4	0.1

[a] 10 psi of $^{13}CH_4$ (0.014 g, 0.87 mmol), ACF (25 mg, 25 µmol) and 0.5 ml of deuterated solvent at 70 ºC. The conversions and TOFs were determined by ^1H NMR spectroscopy using CD_2Cl_2 as external standard and the ratio of deuterated species in the $^{13}C\{^1H\}$ inverse-gated spectrum after 24 hours. The ratios of deuterated products were calculated by integration of individual product signals.

To study the scope of the H/D exchange reaction further, ethane and propane were tested in the presence of C_6D_6. In these reactions, the alkane was bubbled through benzene-d^6 in the presence of catalytic amounts of solid ACF, which was suspended in the NMR tube. Table 2 shows the reaction times and conversions. Ethane and propane underwent H/D exchange giving mixtures that contained a range of deuterated products to yield mono- to fully- deuterated alkanes (SI). No exchange reaction between H_2 and benzene-d^6 was observed.

Table 2. Deuteration of ethane and propane catalyzed by ACF, using benzene-d^6 as deuterium source.

entry	substrate	time (days)	conv/%[a]
1	ethane	4	80
2	propane	4	50

[a] alkanes were bubbled into the reaction solution for 5 min which contained ACF (25 mg, 25 µmol) in 0.5 ml benzene-d^6. The NMR tube was afterwards sealed. The conversions were determined by ^1H NMR spectroscopy using CD_2Cl_2 as external standard in a capillary.

In order to determine potential interactions between ACF and the reactants, CH_4, C_6H_6 and C_6H_{12}, Pulse Thermogravimetric Analyses (*Pulse*TA® P-TGA) were performed (SI). Figure 2 illustrates the experiment in which methane and benzene were alternately exposed to ACF (or an analogous experiment with cyclohexane see SI, Figure S7). The data show that consecutive injections of methane gas do not lead to mass or temperature changes (pulses 1-3 in Figure 2). The subsequent addition of benzene (pulse 4-6) results in mass increase and exothermic responses, demonstrating that the arene undergoes adsorption at the ACF surface. This benzene-modified ACF material does not respond to further injections of methane (pulses 7-9). The *Pulse*TA® experiments support that benzene and cyclohexane (SI, Figure S7) interact strongly with the nanoscopic amorphous ACF matrix,[13a)] whereas methane is not adsorbed. Similar results were obtained for preheated γ-Al_2O_3 (SI, Figure S8).

Interestingly, ACF pre-treated with deuterated or non-deuterated benzene, and which was subjected to vacuum for 48h, did not catalyze the H/D exchange reaction when methane or deuterated methane was exposed to the solids in benzene-d^6 or C_6F_6. Apparently, pre-treating ACF with benzene results in an irreversible blockage of catalytic sited.

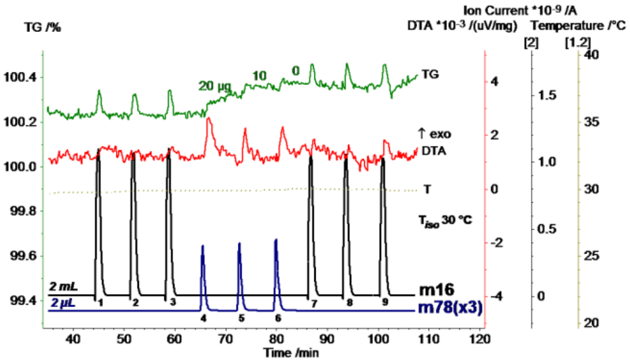
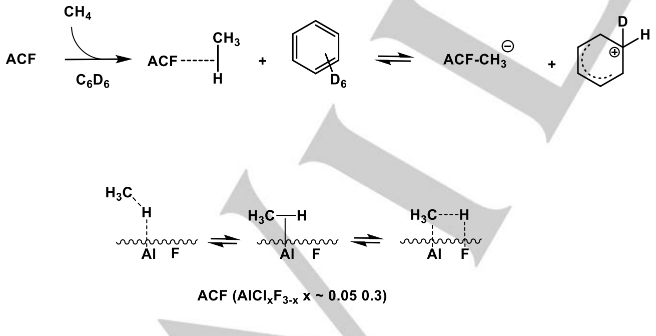


Figure 2. *Pulse*TA® curves of alternating injections of CH_4 (pulses 1-3), liquid benzene (pulses 4-6), and again CH_4 (pulses 7-9) onto 29.3 mg of ACF in Ar. The black and blue ion current curves correspond to the m/z mass numbers of 16 (CH_4^+ for methane) and 78 ($C_6H_6^+$ for benzene).

Mechanistically, we suggest an electrophilic activation of methane at Lewis-acidic aluminum centers at ACF, although the PTA experiments do not indicate any interaction of methane with ACF. However, in solution rapid equilibria involving an adsorption of methane molecules is conceivable. Such an interaction would allow an electrophilic activation of methane and a reversible cleavage of the C–H bond via protonation and benzene-d^6, toluene-d^8 or cyclohexane-d^{12} (Scheme 2).[8b,15] The latter steps are reminiscent of benzonium formation in super acids where C_6H_6 behaves as base to form $C_6H_7^+$ as reported by Olah *et al.* [16] Furthermore, the basic fluorine atoms bound at the ACF surface could support an electrophilic C-H activation of methane and shuttle protons to the solvent molecule.[17] Comparable reaction pathways have been suggested for methane activation reactions at zeolites.[18] The C–H activation of methane at preheated γ–Al_2O_3 is enabled by surface Lewis acid-base pairs. [8c]

The generation of species with methenium-like character at the ACF surface is less likely, because for H/D exchange at benzene or toluene the formation of the Friedel-Crafts products was not observed. Note that ACF can catalyze Friedel-Crafts-type reactions.[13] It should also be noted that ACF always contains some Brønsted acidic centers, because the surface immediately interacts with adventitious water. It therefore can't be entirely excluded that any surface protons may be involved in any H/D exchange reaction by protonation of anionic like methyl groups. The protonation of methane to yield methonium-like species would presumably produce H_2, which was not observed. However, when wet benzene-d^6 was used as solvent in a catalytic set-up with CD_4 incorporation of hydrogen atoms of the water into the methane was observed, but not into benzene. This demonstrates that the ACF surface can induce an H/D exchange between very small amounts of water and methane. The conversions resemble electrophilic methane activation and H/D exchange reactions between methane and Brønsted centres at some zeolites.[19] However, importantly, a catalytic H/D exchange between CH_4 and C_6D_6 in wet C_6D_6 was also oberved. Note, that with larger amounts of water ACF becomes irreversibly destroyed.[20]



Scheme 2. Mechanistic proposal for the H/D exchange reaction between methane and benzene-d^6 catalyzed by ACF; possible coordination modes of methane at ACF.

In conclusion, we showed that nanoscopic Lewis Acidic Aluminium Chlorofluoride (ACF) exhibits an exceptional capability for the activation of C–H bonds in methane resulting in H/D exchance reactions between deuterated aromatics or cyclohexane-d^{12}. $AlCl_3$, $AlBr_3$, HS-AlF_3, γ-Al_2O_3 and preheated γ-Al_2O_3 do not show such a reactivity under the same conditions. Mechanistically an electrophilic activation of methane is presumed at the Lewis-acidic surface sites, although the binding properties of benzene are better than those of methane.

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Keywords: aluminum • fluoride • methane • heterogeneous catalysis • H/D exchange reactions

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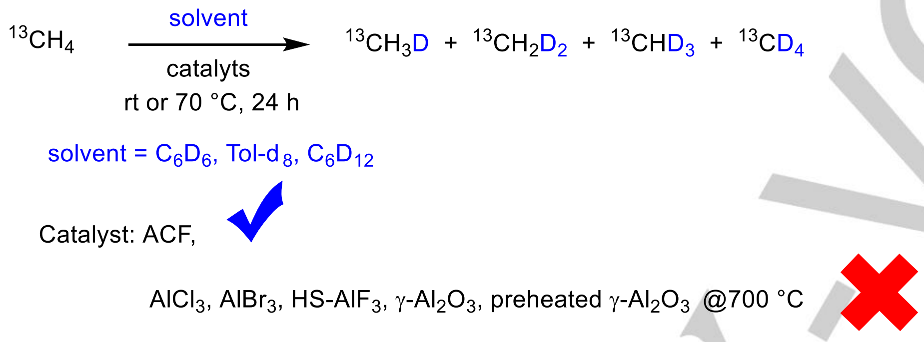
Entry for the Table of Contents (Please choose one layout)

Layout 1:

COMMUNICATION

Nanoscopic aluminium chlorofluoride (ACF) exhibits an excellent catalytic activity in the H/D exchange reaction of CH_4 and deuterated arenes or cyclohexane that results from the interaction of strong Al Lewis acid centers and the reactants at the ACF surface.



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H/D Exchar Reactions of Metha with Aromatics a Cyclohexane Catalyzed by Nanoscopic Alumin Chlorofluoride